

ROUTING AND ACTION

MEMORANDUM

ROUTING

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ACTION TAKEN BY DIVISION

(x) Report has been reviewed for technical sufficiency and IS ☒ IS NOT ☐ satisfactory.

() Material has been given an OPSEC review and it has been determined to be non sensitive and, except for manuscripts and progress reports, suitable for public release.

(x) Performance of the research effort was accomplished in a satisfactory manner and all other technical requirements have been fulfilled.

(x) Based upon my knowledge of the research project, I agree with the patent information disclosed.

Approved by SSL\PANI.VARANASI on 2/21/14 11:55AM

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14. ABSTRACT The goal of the DARPA Local Control of Materials Synthesis (LoCo) program is to develop a generally applicable low-temperature process for the deposition of thin films, whose current minimum processing temperature exceeds the damage threshold temperatures of substrates of interest to the DoD. Early in the program, the representative thin film material was designated to be diamond. Conventional CVD diamond deposition requires temperatures greater than ~ 700 °C, which results in severe degradation of many substrates of interest. To address this challenging scientific and technological problem, we have identified a novel approach. In this approach					
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Room Temperature Deposition Processes Mediated By Ultrafast Photo-Excited Hot Electrons

ABSTRACT

The goal of the DARPA Local Control of Materials Synthesis (LoCo) program is to develop a generally applicable low-temperature process for the deposition of thin films, whose current minimum processing temperature exceeds the damage threshold temperatures of substrates of interest to the DoD. Early in the program, the representative thin film material was designated to be diamond. Conventional CVD diamond deposition requires temperatures greater than ~ 700 °C, which results in severe degradation of many substrates of interest. To address this challenging scientific and technological problem, we have identified a novel approach. In this approach, wavelength specific, femtosecond laser pulses are used to control material processes, particularly growth processes, at the quantum level. Such an approach arises out of a focus on fundamental issues of non-equilibrium many-body physics that have been only recently addressed. We are pleased to report that our research team has exceeded the goals outlined for the first phase of the program and have demonstrated high-quality diamond growth at substantially lower temperatures. Our results demonstrate that this unique approach holds great promise for addressing and solving this important problem. Clearly, additional research needs to be carried out to facilitate further development and eventual implementation.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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(c) Presentations

- (1) Room Temperature Deposition Processes Mediated By Ultrafast Photo-Excited Hot Electrons, N. Tolk, J.Davidson, W. P. Kang, R. Mu, LoCo Kick-Off Meeting, Arlington Virginia, February 27-28, 2013
- (2) Room Temperature Deposition Processes Mediated By Ultrafast Photo-Excited Hot Electrons, N. Tolk, J.Davidson, W. P. Kang, R. Mu, LoCo DARPA Meeting, Golden Colorado April 22-24, 2013
- (3) Room Temperature Deposition Processes Mediated By Ultrafast Photo-Excited Hot Electrons, N. Tolk, J.Davidson, W. P. Kang, R. Mu, LoCo Meeting, Key West Florida, June 24-27, 2013
- (4) Room Temperature Deposition Processes Mediated By Ultrafast Photo-Excited Hot Electrons, N. Tolk, J.Davidson, W. P. Kang, R. Mu, LoCo Meeting, August 14-15, 2013

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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Number of Manuscripts:

Books	
Received	Paper
TOTAL:	

Patents Submitted

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Patents Awarded

Awards

Graduate Students

NAME	PERCENT SUPPORTED	Discipline
Mesut Yilmaz	0.47	
Joy Garnet	0.42	
Justin Gregory	0.04	
Shao-Hua Hsu	0.15	
Zeynab Jarrahi	0.16	
FTE Equivalent:	1.24	
Total Number:	5	

Names of Post Doctorates

NAME	PERCENT SUPPORTED
Justin Gregory	0.34
Halina Krzyzanowska	0.18
William Paxton	0.27
FTE Equivalent:	0.79
Total Number:	3

Names of Faculty Supported

NAME	PERCENT SUPPORTED	National Academy Member
Norman Tolk	0.07	
Jim Davidson	0.63	
Weng P. Kang	0.17	
Richard Mu	0.04	
FTE Equivalent:	0.91	
Total Number:	4	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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FTE Equivalent:

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Names of Personnel receiving masters degrees

<u>NAME</u>

Total Number:

Names of personnel receiving PHDs

<u>NAME</u>

Justin Gregory

Total Number:

1

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
-------------	--------------------------

Mickey Howell

0.13

FTE Equivalent:

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5a: Norman Tolk

5f-1a: Vanderbilt University

5f-c: 6300 Stevenson

Nashville TN 37235

5a: Weng P Kang

5f-1a: Vanderbilt University

5f-c: 6300 Stevenson

Nashville TN 37235

5a: Jim Davidson

5f-1a: Vanderbilt University

5f-c: 6300 Stevenson

Nashville TN 37235

5a: Richard Mu

5f-1a: Vanderbilt University

5f-c: 6300 Stevenson

Nashville TN 37235

Scientific Progress

Technology Transfer

Room Temperature Deposition Processes Mediated By Ultrafast Photo-Excited Hot Electrons

DARPA/ARO Final Report

Norman Tolk,¹ Jim Davidson,¹ Weng Poo Kang,¹ Richard Mu^{1,2}

¹Vanderbilt University, Nashville, TN

²Fisk University, Nashville, TN

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Room Temperature Deposition Processes Mediated By Ultrafast Photo-Excited Hot Electrons

DARPA/ARO Final Report

*Norman Tolk,¹ Jim Davidson,¹
Weng Poo Kang,¹ Richard Mu^{1,2}
¹Vanderbilt University, Nashville, TN
²Fisk University, Nashville, TN*

1. Introduction

The goal of the DARPA Local Control of Materials Synthesis (LoCo) program is to develop a generally applicable low-temperature process for the deposition of thin films, whose current minimum processing temperature exceeds the maximum temperature which substrates of interest to the DoD can withstand. We are pleased to report that our research team has met and exceeded the goals outlined for the first phase of the program. Early on in the program, the representative thin film material was designated to be diamond primarily because of its intrinsically superior properties. Conventional CVD diamond deposition requires temperatures greater than ~ 700 °C, which results in severe degradation of many substrates of interest. In our successful proposal to DARPA, we outlined a novel approach to meet this challenging scientific and technological problem. In this approach, femtosecond laser pulses are used to control material processes, particularly growth processes, at the quantum level. Such an approach to materials science goes beyond traditional investigations of equilibrium processes and focuses instead on fundamental issues of *non-equilibrium many-body physics* that have only been recently addressed. Indeed, achieving low temperature, high-quality films requires that *non-equilibrium* ways to promote the growth of coatings that would otherwise require sustained thermal energy be found.

We proposed in the initial phase to facilitate low temperature growth by applying *in situ* ultrafast optical excitations to the substrate surface during hot filament chemical vapor deposition (HF-CVD). Vibronic coupling between photo-excited hot electrons and surface-adsorbed reactants, and direct substrate-molecular phonon coupling, will induce adsorbate vibrational excitations leading to enhanced surface diffusion and a lowering of reaction energies on picosecond timescales. Conceptually, this vibrational coupling replaces the vibrational motion normally generated thermally in conventional processes, without a significant long-term bulk temperature rise in the substrate. This approach is based on the well established desorption induced by electronic (DIET) and multiple electronic transitions (DIMET) processes where it has been demonstrated that photo-excited hot electrons mediate surface diffusion and surface femtochemistry, and induce desorption of adsorbed atoms and molecules.

During the short time (9 months) that we were a part of the LoCo program, we met and exceeded our time-line schedule and goals and accomplished the following:

- Successfully assembled a team of graduate students, postdocs and senior researchers adept in both laser and CVD deposition science to address the challenge.
- Met and communicated with non-Vanderbilt team members regularly, arranged collaborations as the program went forward.
- Successfully built a dedicated HF-CVD/laser diamond growth system.
- Successfully utilized the system to demonstrate low-temperature growth of diamond on silicon and diamond substrates.
- Discovered a previously unknown effect: laser pretreatment of substrates can promote nucleation and growth without conventional pretreatments such as “seeding”.
- As predicted by our conceptual electron excitation model, successfully demonstrated that laser interactions at greatly reduced temperatures ($\sim 400^{\circ}\text{C}$) that can promote diamond growth depending on photon energy and intensity on single crystal diamond and silicon substrates

2. Conceptual background

To study room temperature chemical vapor deposition (CVD) processes under femtosecond optical excitation, our work primarily relies on the integration of an ultrafast pulsed laser source with a hot filament CVD (HF-CVD) reactor. The femtosecond optical pulses will photo-excite transient hot electrons in the near surface region of the substrate while growth kinetics occurs. On a timescale of a few picoseconds immediately following each optical pulse, these hot electrons will interact with surface molecules and adsorbates via vibronic coupling, as well as through direct lattice-adsorbate phonon coupling thereby enhancing surface diffusion and reducing reaction energies. Assessing and carrying out these experiments requires an understanding of light-matter and electron-phonon interactions in films. Thus, the approach may be assessed by identifying the underlying physics and demonstrating that it meets the necessary timeframes and objectives set forth by DARPA. Conceptually this includes the initial photo-excitation process, hot electron-mediated growth reactions, a case study assessing the advantages and limitations in a model system (carbon films grown on Si(100) surfaces), and identifying quantification measures that will define “successful” enhancement of the films. Schematically this idea is shown in Figure 1.

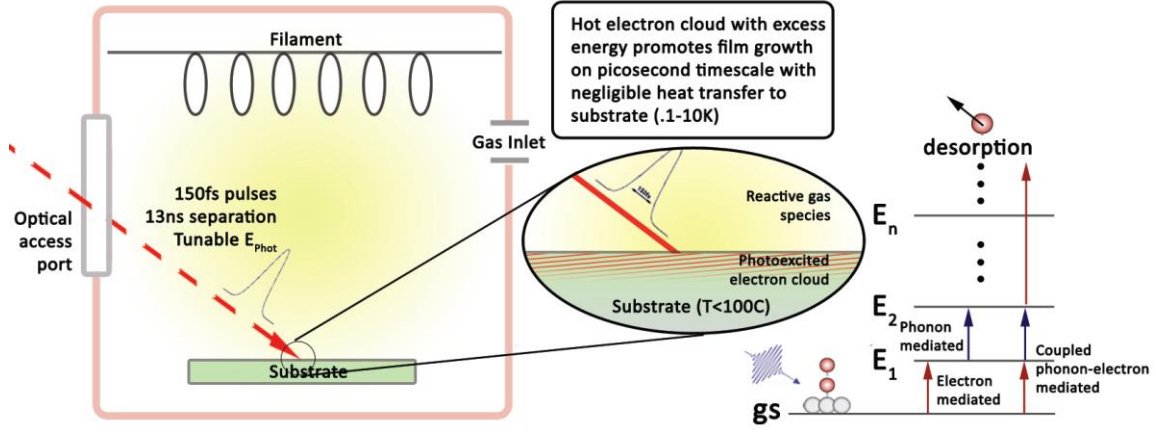


Figure 1. Illustrative description of optically-excited surface kinetics during the CVD process. Generation and evolution of photo-excited electrons at the growth interface.

While photo-excitation of charge carriers by femtosecond optical pulses is a well-understood process [1, 2], its application to *in situ* growth requires understanding of carrier dynamics as a function of laser parameters and in relation to various material optical properties. Fundamentally, photo-excitation involves electronic excitations via the absorption of a photon. Primary absorption mechanisms may differ between metals and dielectrics, e.g. in the former free-carrier or plasmonic excitations dominate the absorption process while in the latter electron-hole pairs are created. Therefore, the criterion $E_{ph} \geq E_g$ must be met to generate hot electrons in semiconductor or insulating materials.

Charge carrier dynamics in semiconductor films can be described in four timescales: initial excitation (τ_0), electron thermalization (τ_1), energy transfer to the lattice (τ_2), and lattice heat diffusion (τ_3). Generation of charge carriers during τ_0 may be considered instantaneous. That is because in this case, $\tau_0 \ll \tau_{pulse}$, where τ_{pulse} is the temporal width of the optical pulse. Immediately following τ_0 the excited momentum distribution can be approximated as a delta function before thermalization and dephasing through electron-electron scattering [3, 4]. The electron system can be conceptualized as a ‘hot’ Fermi distribution centered around an average temperature of 100–1000 K (or greater) depending on laser fluence. During τ_2 (~1–10ps), the hot carrier system begins to lose energy through electron-phonon interactions, with excess carrier energy transferred to the substrate as heat [5, 6]. The rate at which this occurs is determined by the electron-phonon coupling constant (λ_{el-ph}). On much longer timescales, τ_3 , the electrons (holes) rest at the bottom (top) of the conduction (valence) band, and the heat diffuses out of the excitation volume according to the thermal diffusivity of the material.

Considering this, τ_2 defines an “interaction window” prior to reaching thermal equilibrium with the lattice during which hot electrons and hot phonons couple quantum mechanical through resonant energy transfer. The average electron temperature (T_{el}) during τ_2 evolves as energy is lost through optical and acoustic phonon interactions, causing T_{el} to decrease and T_{latt} (the lattice temperature) to increase. Although τ_2 is quite short, the use of high repetition rate lasers allows us to provide this window of interaction millions of times per second. It should also be noted that although T_{el} can exceed 100–1000°C, the peak change in T_{latt} is on the order of 1°C due to the different heat capacities of the electron and phonon systems [7]. Strictly speaking, traditional heat capacity is less

well-defined during excited quasi-equilibrium in semiconductors [8], but is captured conceptually by such descriptions. In general, substrates with decreased electron-phonon coupling, which results in extended τ_2 windows, are more likely to be successful under the proposed growth enhancement mechanism.

Photo-excitation in metals is generally more straightforward due to the presence of equilibrium free carriers. The primary absorption mechanism is free carrier excitation, usually in the form of plasma oscillations when $E_{ph} \geq E_{plasma}$, where E_{plasma} is the energy associated with the plasmonic frequency of the metal. However, photo-excited hot electrons generated by sub-plasmon-frequency photons will still participate in surface kinetics as demonstrated extensively in desorption induced by (multiple) electronic transition studies (DIET/DIMET) and photo-enhanced surface reaction studies [9-13]. We therefore expect our approach to apply equally to metal or semiconductor systems, with each system defining the appropriate laser input parameters.

In situ photo-excitation during an HF-CVD process presents a number of additional challenges to consider. The basic requirement is that hot electrons be present at the growth interface in sufficient density to interact with surface molecules. After nucleation, as growth proceeds, the growth interface will move away from the initial optical excitation volume. In cases where the forming layer has significantly different optical properties than the substrate, the laser parameters must be altered during growth to ensure the excitation volume remains near the growth interface, and such dynamic switching would need to be determined empirically. Carrier diffusion and defect charge trapping may play significant roles in reducing available hot electrons, and the near-surface hot electron density may be significantly lower than the excited volume. This may require laser intensity beyond the range of an oscillator system (nJ/pulse), and require an amplifier capable of μ J/pulse. Conversely, μ J/pulse energies will increase substrate temperatures significantly and may lead to non-thermal ablation of the film itself. These issues must be addressed in subsequent phases of our research.

Here we consider the interaction between the laser induced electron cloud and the surface adsorbates, and assess its impact on growth kinetics. The strong coupling between photo-excited electrons and phonons and surface molecular vibrational resonances has been well-established and much effort has been directed towards desorption induced by electronic transitions (DIET), multiple electronic transitions (DIMET), and other photo-stimulated surface kinetics [9-22]. The driving force of the observed photo-induced reactions has been attributed to hot electron-mediated adsorbate motion. Here hot electrons either transfer energy quantum mechanically to resonant adsorbate excited states, or the adsorbates couple directly to phonon excitations of the substrate [23]. The sum of this transient, non-equilibrium energy transfer induces reactions that are otherwise not energetically favorable. An excellent example of this phenomena was provided by Bonn, *et al.* [21], in observing that femtosecond optical excitation of co-adsorbed CO molecules and atomic oxygen resulted in the formation of CO₂, whereas thermal heating resulted only in desorption of CO molecules.

Such results point to hot electron-mediated surface reactions as a route to controlled non-equilibrium femtochemistry [14, 17, 20]. Precise interactions, coupling mechanisms, and reaction yields have been investigated both experimentally and theoretically for a variety of systems [9, 11, 18]. Notably, highly nonlinear photo-desorption yields and enhanced quantum efficiency for desorption of NO from a Pt(111)

surface was observed under femtosecond optical irradiation and later attributed to hot electron-adsorbate interactions [9, 12]. Surface diffusion of atomic oxygen along vicinal Pt(111) was also attributed to hot electron-mediated bond breaking on picosecond timescales [13].

Of particular interest to the application of this approach to the nucleation and growth of carbonaceous films, photo-excited hydrogen desorption from graphite (0001) was observed to follow power laws seen in earlier DIMET studies and was attributed to reaction pathways opened by hot electron coupling with adsorbed hydrogen [22]. The photo-excited hot electrons couple strongly enough to overcome reaction energy barriers (0.25 eV for graphite (0001)) is encouraging for their application to SOA CVD processes, wherein hydrogen plays a significant role in reaction chemistry [24-28].

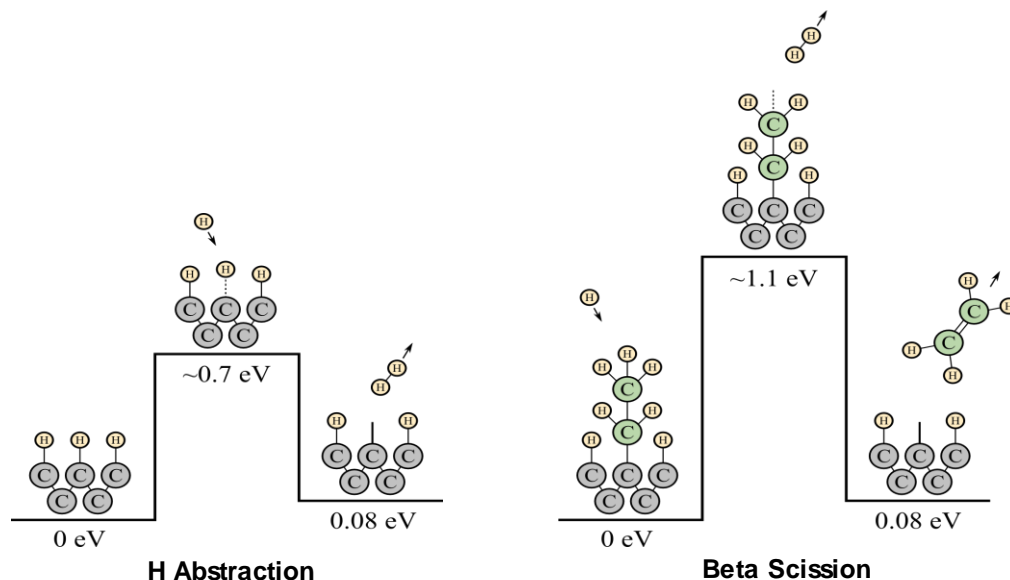


Figure 2. Two critical surface reactions needed to start diamond growth [29].

It is apparent that the surface of diamond in the growth environment is very active with the abstraction of each surface hydrogen generating a vacant site 70 μ s (on average), and the refilling of the site 15 μ s later, allowing for the potential of surface hydrogen hopping or vacancy diffusion along certain directions, and relatively short mean distances between adjacent vacancies. One pathway leads to the desorption of ethylene (C₂H₄) via a beta-scission reaction after the abstraction of a hydrogen atom (see Fig. 2) [30]. With a help of an ultrafast laser set, our preliminary results reveal that we may stimulate the diamond growth using femtosecond pulses. The scheme of reactions, which occur during on the diamond's surface during the growth is depicted in Fig. 3.

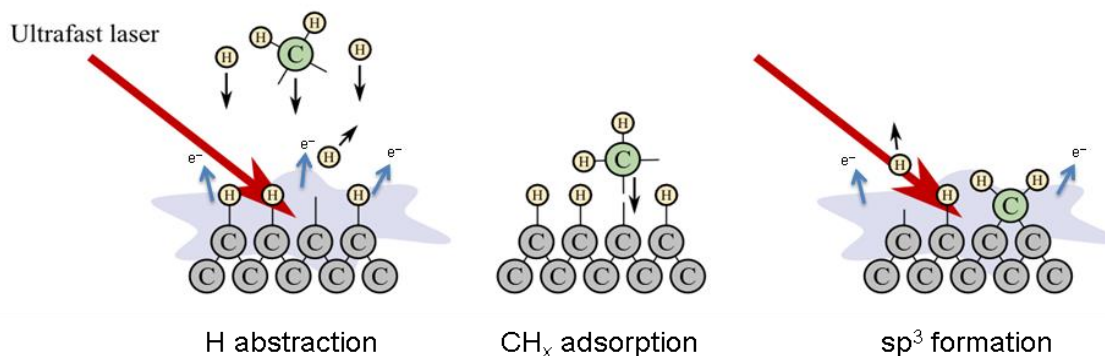


Figure 3. Laser induced electrons assist in abstracting H to reveal reaction sites resulting in CH_x adsorption sp³ formation.

Bridging the gap between desorption and reactions at the growth interface represents a significant advance in complexity, because (a) it requires knowledge of the exact vibrational kinetics of the desired reaction pathway and (b) we need to achieve the electronic transitions of the DIMET process without causing total desorption. Determination of reaction pathways, even for simple vibronic energy transfer leading to desorption of diatomic molecules, relies on density functional theory and potential surface calculations, which are often approximated in light of experimental results. Demonstrating proof-of-principle observation within the project base phase requires a coupled experimental-phenomenological approach where experiment informs the theoretical component and modeling is used for parameter optimization. Our modeling efforts considered optimization of laser input parameters by calculating transient electron dynamics, hot electron densities at the surface, and the time-evolution of electron temperature and concentrations.

3. Results and discussion

3.1 Experimental configurations and technical progress:

During the initial phase (9 months) of the DARPA LOCO project, we designed, constructed, and implemented a highly versatile HFCVD diamond deposition reactor and sample holder, which allowed easy access for incoming and outgoing laser beams as shown pictorially in Figure 4. This system is described in detail in **Appendix A**.

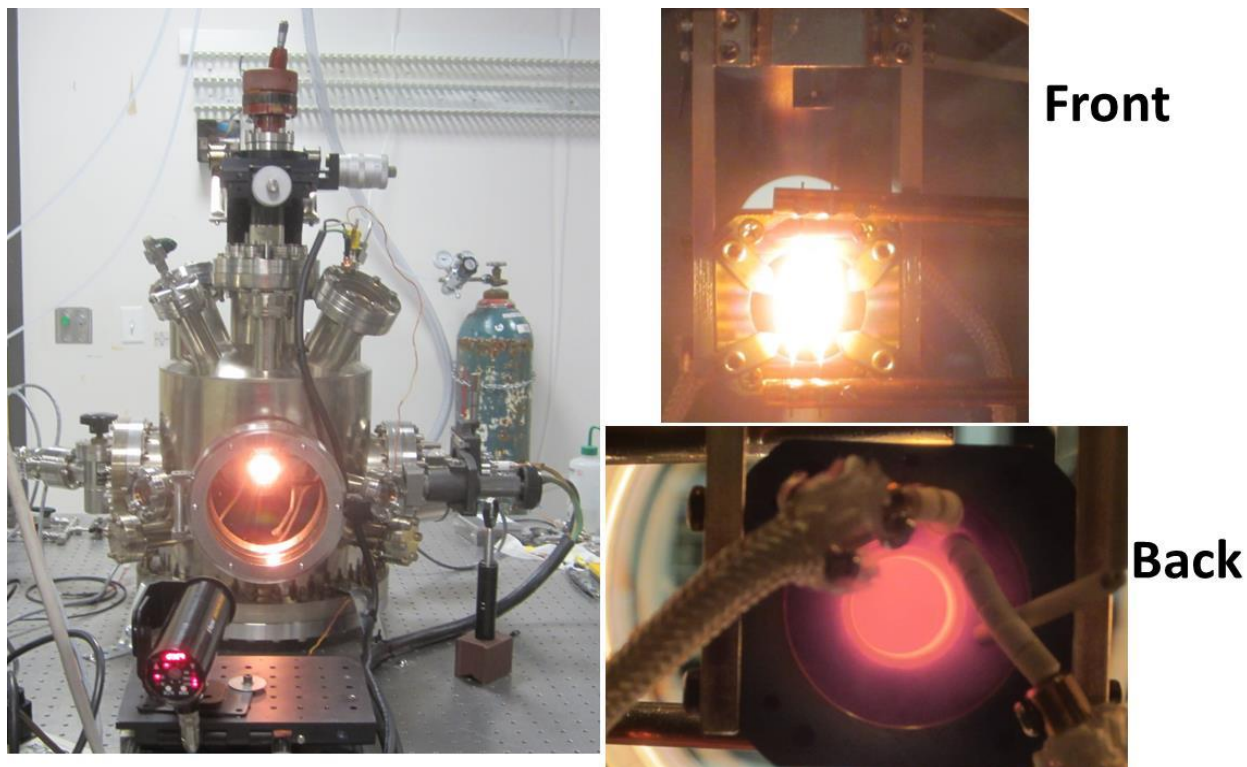


Figure 4. *LoCo HFCVD reactor under operation.*

Baseline deposition conditions for the HFCVD system followed typical CVD pressures of methane and hydrogen, substrate temperature, filament temperature, and filament distance for CVD processing. Specific conditions for executed trials are noted in each relevant data figure, where it is seen that the methane flow was $\sim 1\%$ of hydrogen flow, and pressure circa 30-50 Torr. Variables of specific interest were substrate temperature, laser wavelength and intensity.

3.2 Procedure for the determination of surface modification thresholds: Optimal power and substrate temperature

Preliminary testing was performed to establish at what laser intensity physical damage to the silicon substrate would arise. Our intent was to establish threshold levels for laser induce damage. Given this, we endeavored to execute deposition trials below damage value. As shown in Figure 5 we established that the intensity should be $\sim < 100\text{GW}/\text{cm}^2$. It is apparent that at $132\text{ GW}/\text{cm}^2$ there was significant disruption of the surface.

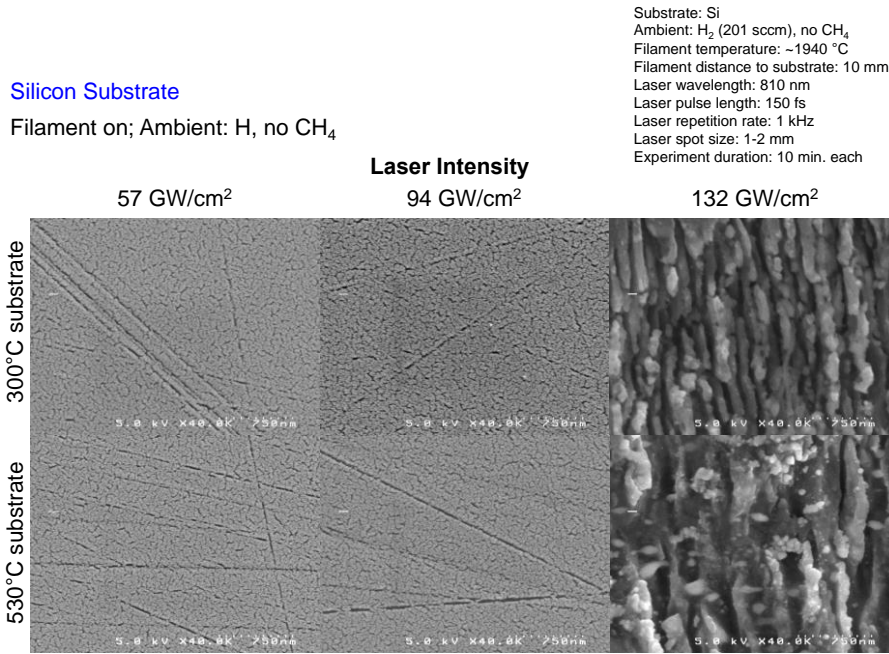


Figure 5. Substrate modification and damage assessed as a function of laser intensity.

3.3 Laser pre-treatment of surfaces is found to influence nucleation and growth: in-situ laser exposure enhanced nucleation and growth found to be dependent on photon energy .

One significant advantage of our technique is the elimination of the need to pretreat the substrate prior to deposition. Most commonly, the heteroepitaxial deposition of diamond requires abrading the substrate surface as diamond growth occurs most favorable at defect sites [31, 32]. Further pretreatment typically involves nucleating the surface with nanodiamond structures to expedite the deposition time. We have found that modifying the substrate surface through high-power ultrafast excitations can be substituted for these pretreatment steps. In order to demonstrate this phenomenon, we laser irradiated at only predetermined locations on the substrate. Figures 6 and 7 show SEM pictures of the pre-treatment studies, supported by Raman analysis. Thus, we have developed the first known method for the selective heteroepitaxial deposition of diamond patterning, potentially paving the way for an all-diamond integrated circuit.

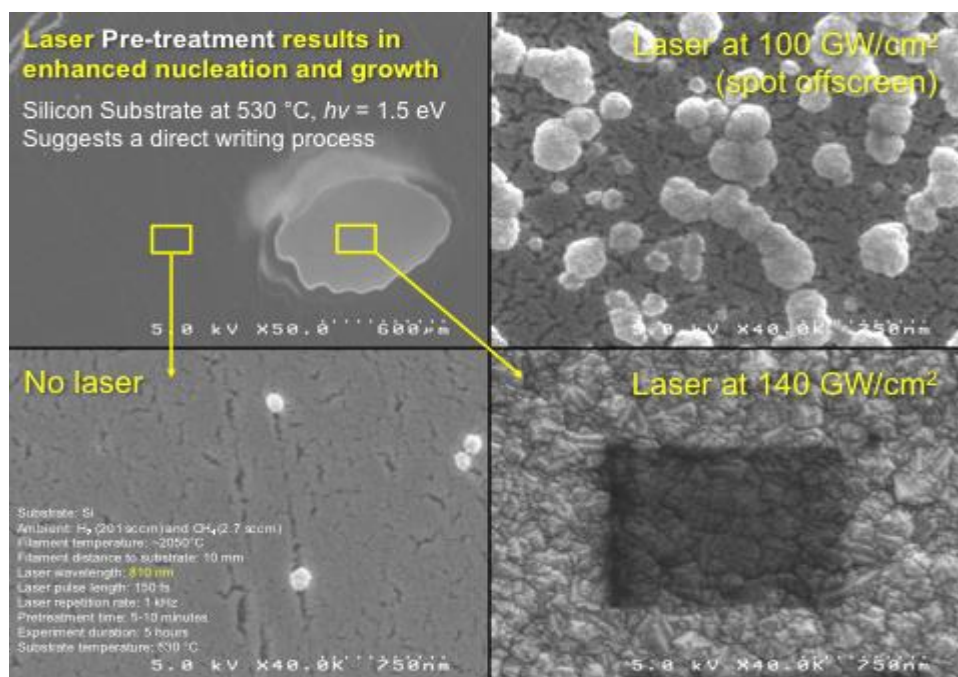


Figure 6. SEM images of diamond films grown on a single-crystal Si substrate, with and without in-situ laser exposure. Significant enhancement of diamond growth is shown.

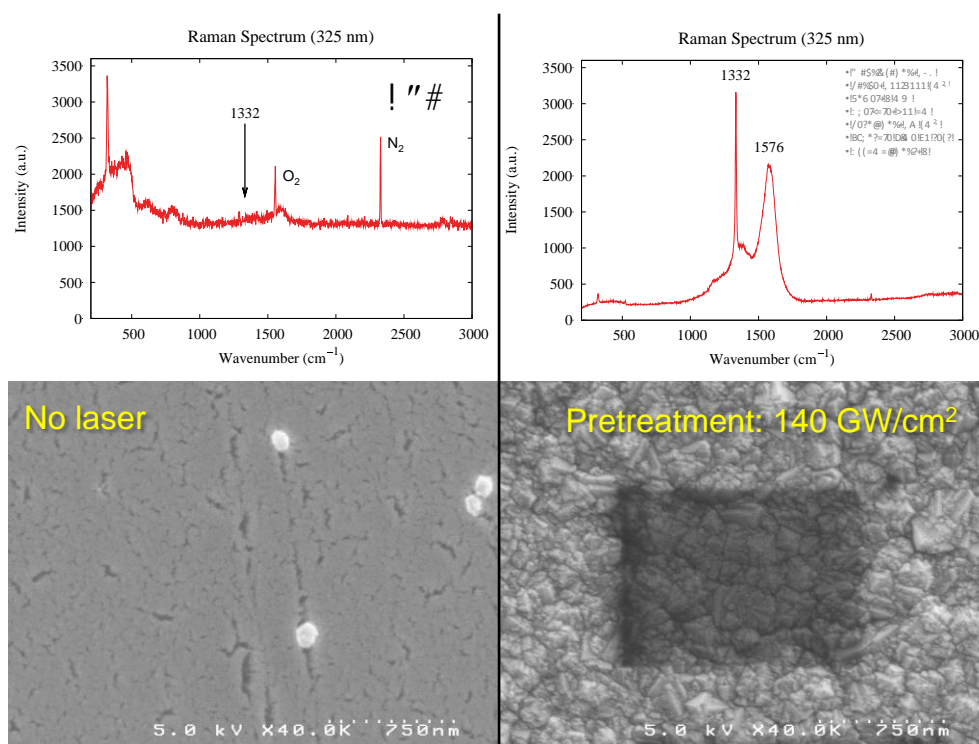


Figure 7. Raman spectra and SEM images of diamond films grown at a temperature of 530°C on a single-crystal Si substrate, with and without in-situ laser exposure. Clear evidence of diamond growth due to laser pre-treatment conditioning is shown in the intensity of the Raman diamond peaks (1332 cm^{-1} and 1576 cm^{-1}).

3.4 Deposition at low temperature with laser enhancement

The numerous material advantages of diamond have enticed many researchers to examine it as a potential alternative to silicon in the semiconductor industry. The major obstacle preventing the widespread use of diamond is the unconventional and often unreliable fabrication methods. Further, a technique to mass-produce diamond wafers, such as the Czochralski method for silicon, has not yet been developed. Our novel approach to diamond deposition utilizing ultrafast laser techniques has the prospect of overcoming many of these hurdles. Figure 8 shows the scheme with comparison of high-temperature (conventional) and low-temperature (laser assisted) growth.

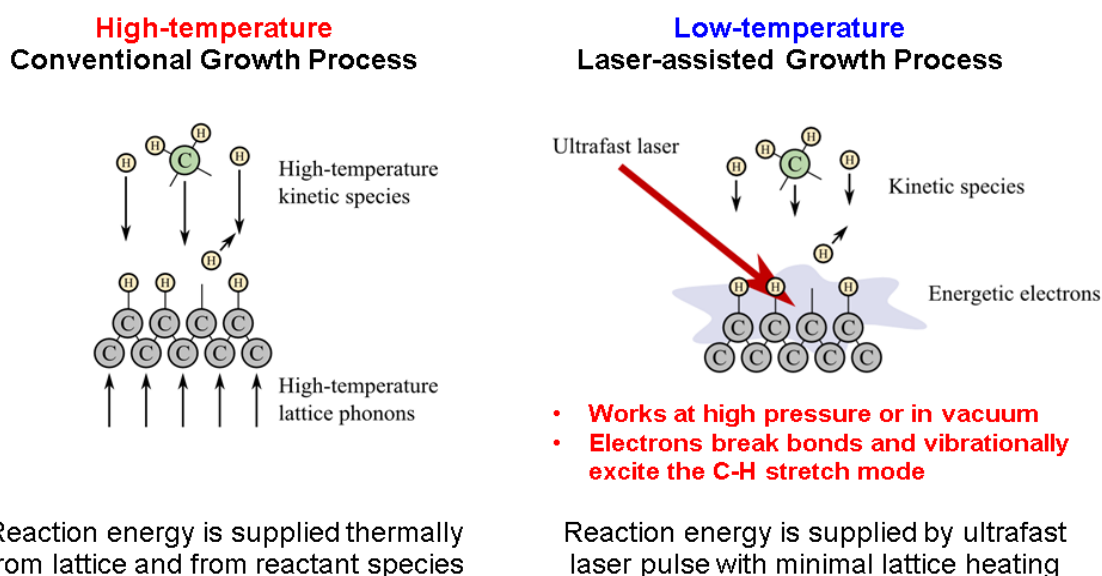
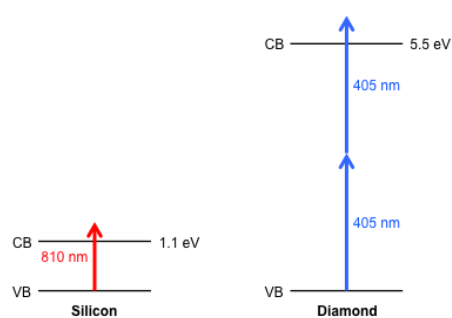


Figure 8. Comparison between conventional high-temperature and low-temperature laser-assisted growth processes.

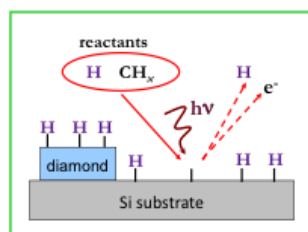
Efficacy of laser-induced electrons on CVD growth depends on substrate band gap



Efficacy of laser-induced electrons on CVD growth depends on substrate band gap

Lasers on Si substrates

$h\nu \sim 1.5 \text{ eV}$ (810 nm), pulse 150 fs, rep. rate 1 kHz



Lasers on diamond substrates

$h\nu \sim 3 \text{ eV}$ (405 nm) or $2 \times 3 \text{ eV}$, pulse 150 fs, rep. rate 1 kHz

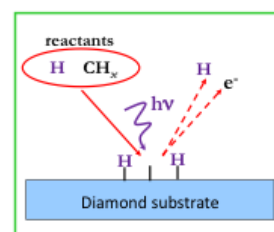


Figure 9. Schematic representation illustrating the importance of selecting photon energy appropriate to a particular substrate, determined by the band-gap of the substrate.

By using 100 fs optical pulses to induce photo-excitation, the hot electron and phonon systems provide an “interaction window” of a few picoseconds during which adsorbate excitations may occur, prior to complete electron-phonon energy transfer in the substrate. The nature of our laser system allows us to meet the following goals: (1) it will provide sufficient driving force for chemical reactions while causing negligible temperature rise in the substrate; (2) photo-excitation of electrons at the growth interface can be easily integrated with parallel enhancement processes; (3) only photon energies sufficient for photo-excitation are required, making this approach applicable to a wide variety of material systems; (4) using standard equipment, hot electron densities and most laser requirements can be met, and proof-of-principle demonstrations can be made.

Chemical vapor deposition (CVD) is a critical state-of-the-art process for the fabrication of thin films and coatings on arbitrary substrates. However, conventional deposition recipes require elevated substrate temperatures ($>800\text{ }^{\circ}\text{C}$) to supply surface reaction energy, which excludes many desirable but fragile substrates from CVD processes.

In this program we have demonstrated enhanced low-temperature (300–400 $^{\circ}\text{C}$) hot filament CVD diamond film deposition on silicon and diamond substrates using ultrafast laser excitation. The requisite surface reaction energy is supplied *non-thermally* by energetic photo-excited electrons, which create reactive sites by desorbing H directly and by the vibrational excitation of the C-H bond thus facilitating H abstraction. This non-equilibrium process results in negligible substrate heating due to the low duty cycle of the pulsed laser.

Enhanced film quality and growth rate have been verified using scanning electron microscopy and Raman spectroscopy. Figure 10 shows the processing conditions and the subsequent diamond growth, *on diamond*, indicating the enhanced growth (more diamond) where the laser was incident on the diamond substrate (left image) in contrast where there was no laser exposure (right image). Given that the SEM images are the same magnification, the laser-enhanced growth is evident.

Laser at 405 nm shows enhanced growth at 430 °C

Single-crystal Diamond Substrate

Substrate: single-crystal CVD diamond
 Ambient: H₂ (201 sccm) and CH₄ (2.7 sccm)
 Filament temperature: ~2050°C
 Filament distance to substrate: 10 mm
 Laser wavelength: 405 nm
 Laser pulse length: 150 fs
 Laser repetition rate: 1 kHz
 Laser power: 100 mW
 Laser intensity: 40 GW/cm²
 Experiment duration: 4 hours
Substrate temperature: 430 °C

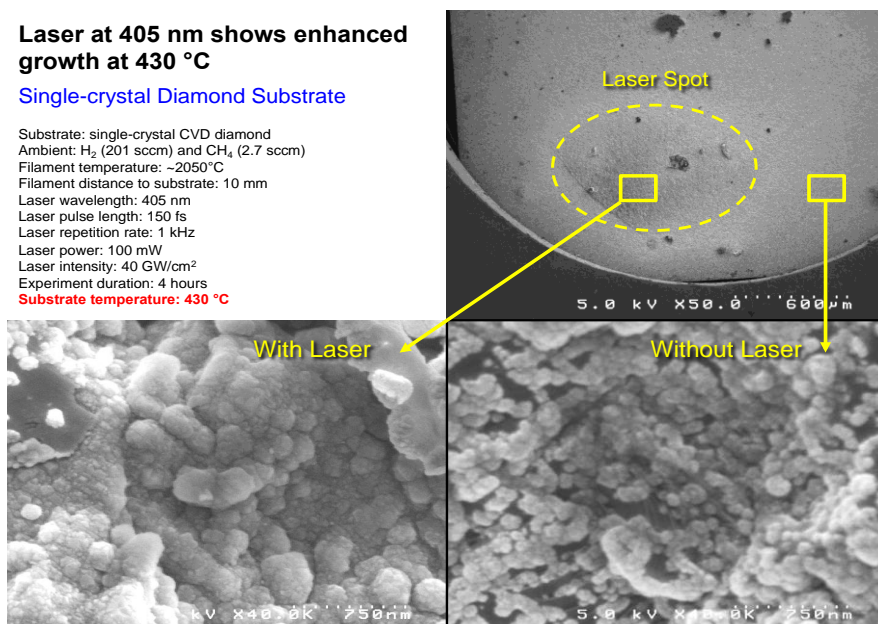


Figure 10. SEM images of diamond films grown on a single-crystal diamond substrate, with and without in-situ laser exposure.

Also relevant to the point, Figure 11 compares the Raman spectra of the with/without laser exposure and the >> sp³ signal from the laser stimulated region implies more diamond.

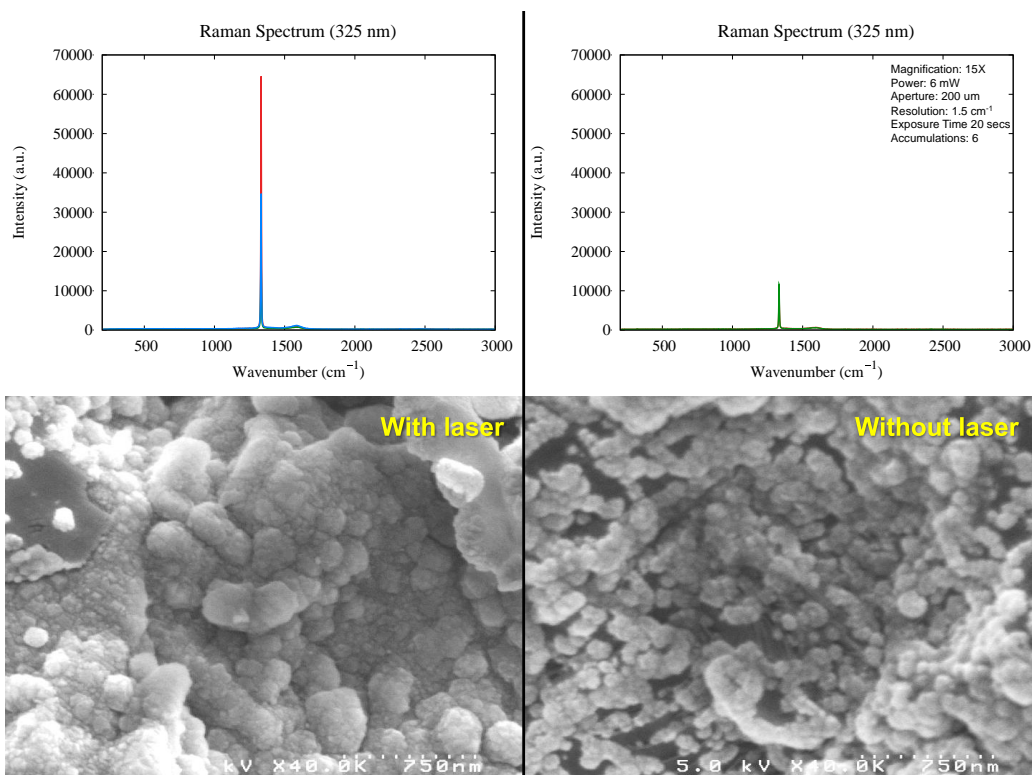


Figure 11. The same SEM images shown in Fig. 12 comparing the Raman spectra of the disparate growth areas with and without laser exposure.

Figure 12 presents the diamond growth outcome laser/no-laser from a silicon substrate. Here again, on a different, non-diamond substrate an increased amount (growth) of diamond (right image) is seen in comparison with no laser exposure. (Process conditions are detailed in the figure).

810 nm laser exposure during growth shows some enhanced nucleation

Silicon Substrate

Due to electrons generated on the silicon but not on the diamond

Substrate: Si
Ambient: H₂ (201 sccm) and CH₄ (2.7 sccm)
Filament temperature: ~2050°C
Filament distance to substrate: 10 mm
Laser wavelength: 810 nm
Laser pulse length: 150 fs
Laser repetition rate: 1 kHz
Laser power: 220 mW
Laser intensity: 80 GW/cm²
Experiment duration: 5 hours
Substrate temperature: 430 °C

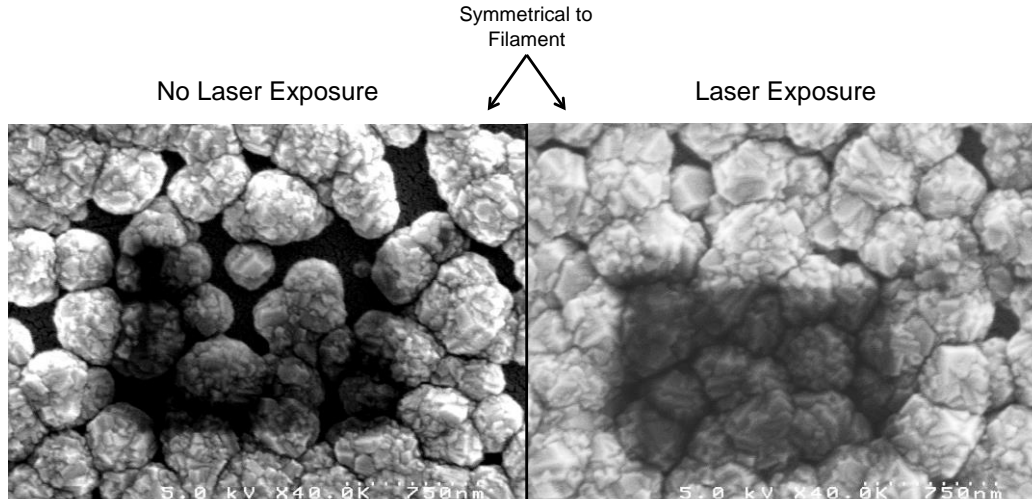


Figure 12. Diamond growth outcome laser/no-laser on silicon substrate.

Still another example of laser influence on diamond growth conditions is illustrated in the results shown in Figure 13. In this deposition experiment, the target substrate was the “backside” of a CVD polycrystalline diamond film/membrane. As in previous measurements, we may compare a region exposed to the laser with another area which was simply exposed to the deposition conditions without laser exposure. As shown in the figure, there is a striking difference between the laser area and the unexposed area. In particular, the average grain size is seen to be (a) more uniform, and (b) significantly smaller than in the non-exposed area.

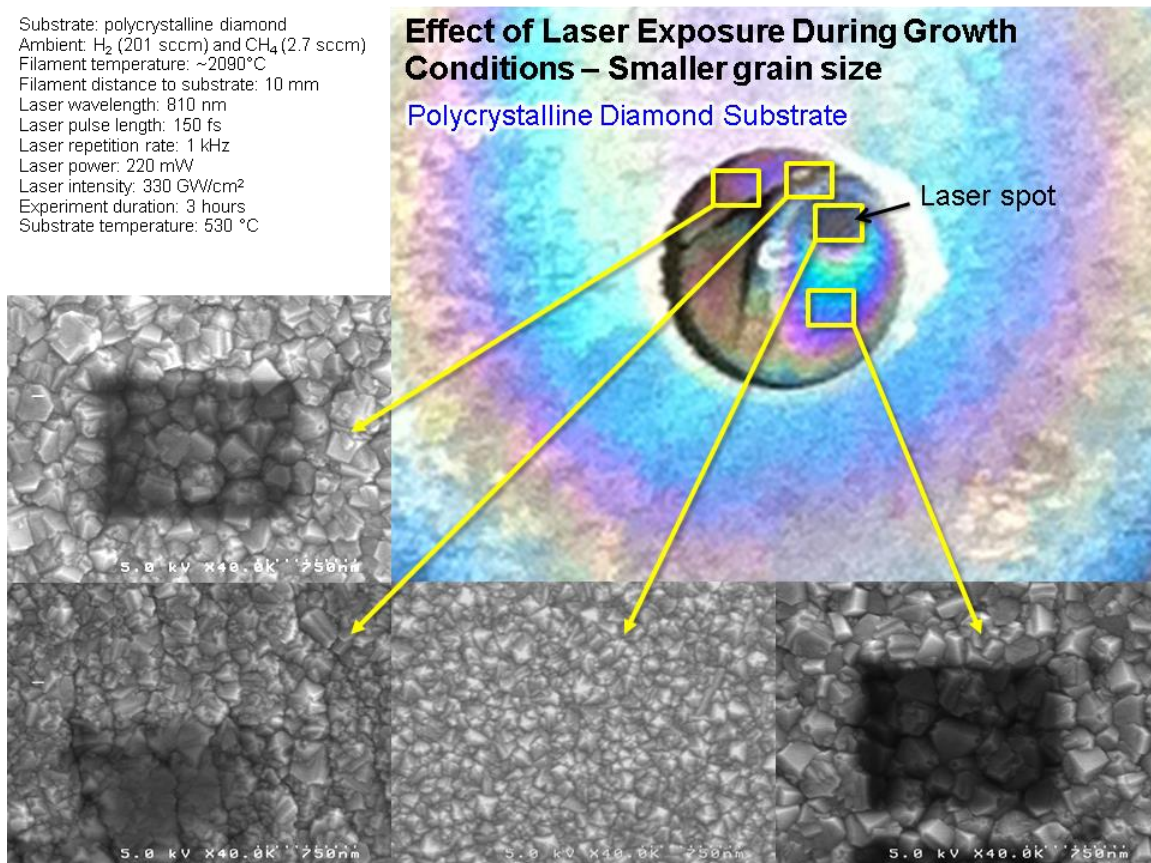


Figure 13. Deposition on 'backside' of a CVD polycrystalline diamond film/membrane.

We intend to build on these exciting preliminary results through further exploration of the effects of laser power, wavelength, and growth conditions on deposition rates and film quality, with the ultimate goal of achieving near room-temperature film growth.

4. Conclusions

We have used ultrafast optical pulses to excite near-surface electrons, plus localized phonons on short timescales that participates in growth kinetics, providing a large reservoir of energy from the photo-excited electrons available to interact with reactant species and enhance surface mobilities through ballistic collisions and acoustic phonons. The large difference in heat capacities between electrons and the substrate leads to negligible temperature rise, providing a means to add energy to the growth reaction kinetics without adding significant temperature. We demonstrated that this vibronic coupling between hot electrons and adsorbates, as well as localized phonons provided excitation energy without substantial

temperature rise, reducing reaction energies and enhancing surface mobility under non-equilibrium conditions. We thus achieved low temperature film growth using transient photo-excitation of hot electrons in situ during CVD processes.

- *We have demonstrated low temperature growth on both silicon (approximately 430°C) and diamond (approximately 530°C) substrates consistent with the proposed model of growth stimulated by laser-induced electrons. By appropriate variations in parameter space we believe that we can accomplish successful growth in the 100 – 200°C range.*
- *In particular, we have shown that in-situ laser exposure enhances nucleation and growth, where photon energies are employed, consistent with the requirement to produce surface electrons from specific substrates, to provide necessary reaction energy.*
- *We have shown that laser pre-treatment of surfaces enhances nucleation and growth.*

5. Work remaining to be done and future directions

The contributions we have made in this short period are encouraging and suggestive. Thus it is important to continue to further this promising line of research.

Specifically, we suggest the following experimental and modeling efforts be carried out:

- Extend growth experiments to lower values in the 100 -300°C range;
- Further examine the mechanisms responsible for enhanced nucleation due to laser pretreatment as a function of laser wavelength and intensity;
- Continue development of sophisticated process modeling based on laser induced electronic excitation;
- Examine the effect of direct resonant laser induced vibrational mode excitation;
- Perform measurements of the H adsorbate vibrational lifetimes (C-H stretch) using laser pump-probe transient bleaching spectroscopy; and
- Experimentally determine the energy distribution of laser induced electron fluxes using a time-of-flight technique.

Our measurements have shown that this research direction holds exceptional promise in providing both fundamental and technical knowledge of substantial impact.

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Appendix A

DETAILS OF THE HFCVD diamond deposition reactor and sample holder

The body of the reactor consisted of a large (~50L), multiport conflate flanged vacuum chamber, Figure A-1a, A-1b. Samples to be tested were mounted on a custom-built heating stage, equipped with a doughnut-shaped, resistive heating element to allow optical access to the backside of the samples (Figure A-2).

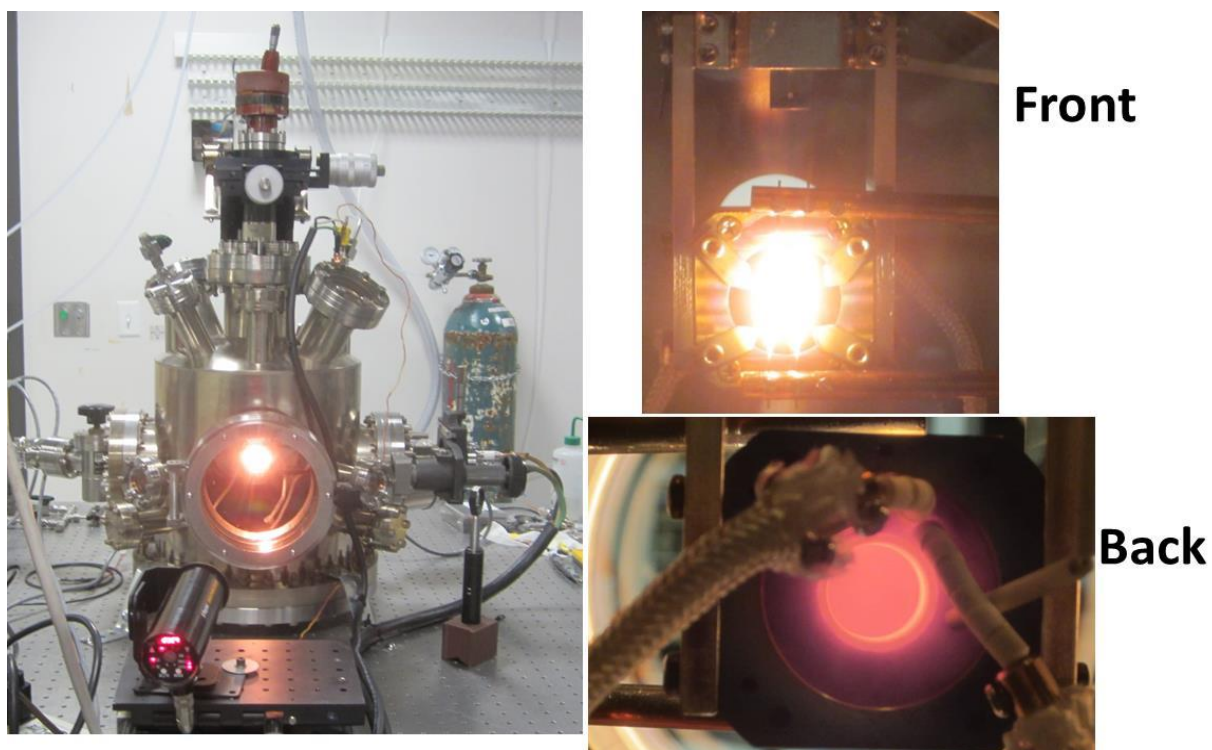


Figure A-1a. Photograph of the LoCo HFCVD diamond deposition reactor.

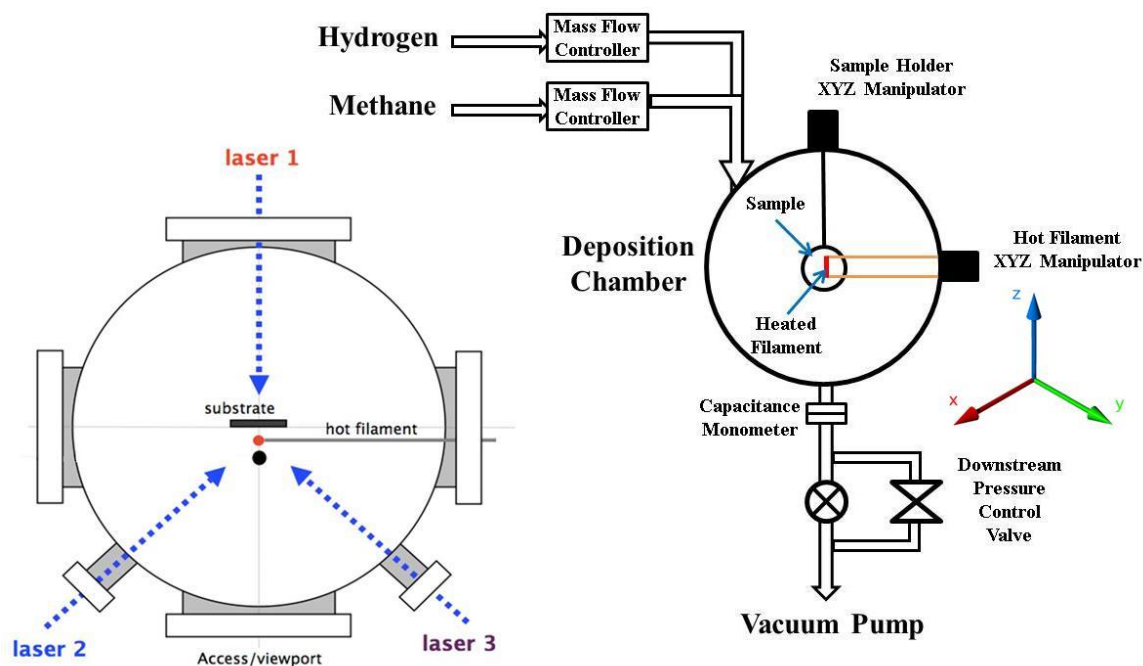


Figure A-1b. Schematic diagram of LoCo reactor.

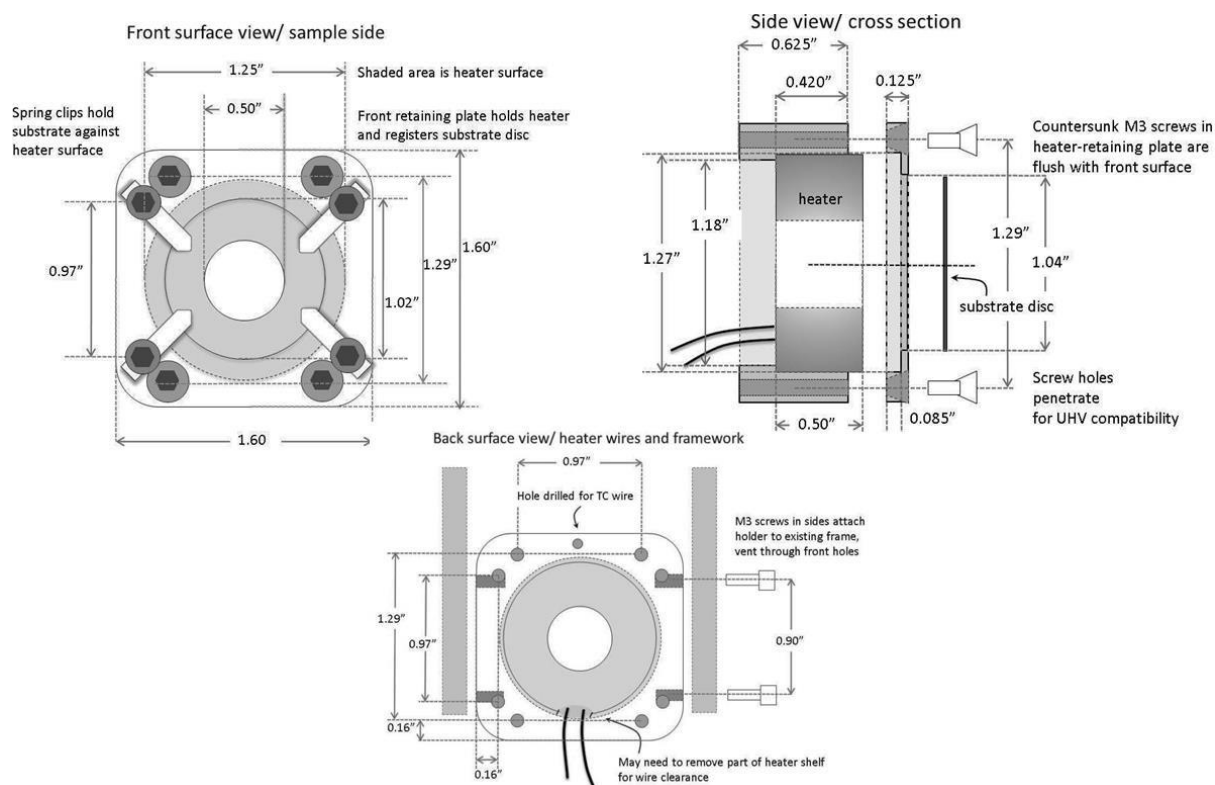


Figure A-2. Custom-built heating stage, equipped with a doughnut-shaped, resistive heating element to allow optical access to the backside of the samples

The sample holder was suspended in the middle of the chamber through a stainless steel rod which extended upwards (along the z-axis) to a multi-axis (x, y, z, and θ) micromanipulator. This configuration allowed for easy maneuvering of the sample. A thermocouple was attached to the back-side of the doughnut heater for observation of the sample temperature. Calibration of the thermocouple temperature with a low-temperature pyrometer indicated only a $\sim 30^{\circ}\text{C}$ temperature gradient between the thermocouple location and the topside of the sample which faced the filament. The hot filament was composed of tungsten wire mounted across two 0.25" diameter copper rods (for electrical connection) which were attached to a second multi-axis micromanipulator (Figure A-1b). This second manipulator allowed the filament position to be translated relative to the sample to achieve the desired growth conditions. Temperature of the filament was constantly monitored by an external two-color pyrometer. During diamond deposition, the filament temperature was held between 2000-2200°C. The reactor's pressure-control system was composed of three primary components: mass flow controllers (MFCs), a capacitance manometer (CM), and a downstream pressure control valve (PCV). The MFCs allowed for desired flow rates of molecular hydrogen and methane (required for diamond growth) to enter the chamber. The pressure in the reactor was constantly monitored with the CM, which allowed for direct pressure measurement, independent of gaseous environment composition. The pressure in the chamber was maintained by a downstream PCV connected directly to the vacuum pump in parallel with an isolation valve.